BP 742,493

BRITISH PLASTICS

PREMIER JOURNAL OF THE PLASTICS INDUSTRY FOUNDED 1929

VOLUME 27 JUNE, 1954 NUMBER 6

Editor: Phillip Morgan, M.A.

ASSOCIATED ILIFFE PUBLICATION

ILIFFE & SONS LTD., DORSET HOUSE, STAMFORD STREET, LONDON, S.E.1

Telephone: *Waterloo* 3333 (60 *lines*) *Telegrams:* *Briplastic, Sedist, London*

Branch offices at Manchester, 260 *Deansgate.* Coventry, 8-10 *Corporation Street.* Glasgow, 26b *Renfield Street.* Birmingham, *King Edward House, New Street*

Annual Subscription: £1 13s. 6d.; U.S.A., $5.50 Canada, $5.00. Published on the 15th of each month

STABILIZERS FOR VINYL POLYMERS

PART 2
METALLIC COMPOUNDS OTHER THAN SOAPS

By H. VERITY SMITH

This is the second part of a survey on the types of stabilizers suitable for vinyl compounds. The first part covering soaps was published last month, and the final section describing organic compounds will be published in our August issue.

IN this survey, the diverse materials used as vinyl stabilizers have been classified into the following main groups: the metallic, the organometallic, and the organic. Soaps, which form the main group of metallic compounds, were dealt with in last month's issue of *British Plastics*.

The remaining metal compounds may be subdivided as follows:—

Inorganic compounds: phosphates and phosphites, per-salts, silicates, and salts of the acids of sulphur.

Organic metal compounds: salts of organic acids, miscellaneous metal derivatives.

Phosphates and phosphites

In view of the known tendency of phosphate plasticizers to diminish the light stability of vinyl resins it is rather surprising to find that many phosphate compounds have been used with success as light stabilizers.

In 1938 a patent was issued to A. B. Japs[1] in respect of the use of *trisodium orthophosphate* (Na_3PO_4) as a stabilizer; this patent also refers to the use of other alkali metals and lead salts of the oxyacids of boron and phosphorus. One of the chief functions of phosphates is the deactivation of iron in vinyl solutions; they can also be used for the deactivation or removal of iron from vinyl emulsion-polymerization systems. An example[2] is the use of a mixture of *tetrasodium pyrophosphate* ($Na_4P_2P_7$) and *sodium hexametaphosphate* $(NaPO_3)_8$ to remove iron from the polymerization system before the emulsion is coagulated for drying. It has also been proposed[3] to add a solution of tetrasodium pyrophosphate to a vinyl latex and spray-dry the mixture. The resulting powder is then used as a readily dispersible stabilizer master-batch for extrusion and moulding compounds. *Tribarium orthophosphate* and tetrasodium pyrophosphate are also used for the stabilization of lightly plasticized vinylidene chloride-vinyl chloride co-polymers[4].

Disodium hydrogen phosphate ($Na_2HPO_4 7H_2O$: sp. gr. 1·679).

This material is quite commonly used as a light stabilizer. The crystalline form is powdered to permit easier dispersion. The anhydrous form would be preferable if it were not for its hygroscopic properties.

Chaban also refers[5] to the use of mixtures of disodium hydrogen phosphate with borate-hydroperoxides in which the phosphate acts as the light stabilizer.

Proprietary brands (U.S.): Vanstay L[6] (mixture with sodium silicate), Victor 85X[7] (88% Na_2HPO_4 + 12% sodium penta capryl tripolyphosphate).

Sodium penta octyl tripolyphosphates ($Na_5(C_8H_{17})_5(P_3O_{10})_2$)

These compounds[8], originally produced as wetting agents, have found commercial application as light stabilizers[9] for transparent vinyl co-polymer stocks. They give great clarity and freedom from "haze," but are inadequate as heat stabilizers and their action must be reinforced by the use of a heat stabilizer such as lead ethyl hexoate or calcium silicate. These compounds also act as dispersing agents for vinyl organosols and have the additional advantage of being non-toxic.

Proprietary brands (U.S.): Victor 53[7] (penta-octyl), Victor 85[7] (penta-capryl), Ferro 541[10], Ferro 541A (anhydrous).

Trimagnesium orthophosphate ($Mg_3(PO_4)_2 5H_2O$)

This is claimed[11] to provide powerful synergetic action as a light stabilizer in conjunction with organotin compounds. *Tricalcium orthophosphate* is also one of the light stabilizers, recommended by Chaban for use with borate-hydroperoxides[5].

Sodium and potassium phosphites

These have also been proposed as stabilizers, and it is stated that they provide light protection superior to that of the more commonly used dibasic lead phosphite. The use of a good heat stabilizer, such as barium ricinoleate, is a necessary condition of the outstanding results which have been claimed[12].

Dibasic lead phosphite ($2PbO.PbHPO_3.\frac{1}{2}H_2O$: sp. gr. 6·94)

This is one of the best of the basic lead stabilizers, and the most commonly used phosphorus stabilizer. It is a good acid acceptor, has mild anti-oxidant properties and as in excellent ultra-violet screen, though being opaque also to visible light, it is only suitable for opaque vinyl compounds. Its manufacturers claim[13] that it is capable of reaction with polyenes and thus inhibits colour formation in heat-degraded p.v.c., but no theory of its dienophilic action is advanced.

Proprietary brand (U.S.): Dyphos[14].

Per-salts

In 1945 Chaban introduced the perborate-hydroperoxide stabilizers[15] of the type $NaBO_2.H_2O_2.3H_2O$. These substances are claimed to interact with the polymer, in such a way as to reduce the water-solubility of the alkali perborates and to improve the toughness and abrasion-resistance of the polymer, raise its thermal yield-point and improve the dryness of "hand" of film, etc.

Many of the "Stabelan" products are based on a patent of 1950[5] which describes the use of the borate-hydroperoxides and other per-salts in conjunction with phosphates. Examples include Stabelan E and XL[16]. No justification for the use of a powerful oxidizing agent as a stabilizer for an oxidation-sensitive material such as heat-degraded p.v.c.

is put forward. Another "oxidizing" stabilizer is described by Mouchiroud, who discloses[17] the use of *sodium dichromate*, used in small doses of from 0·01 to 0·1 part per hundred of polymer, as a light stabilizer for unplasticized foils and filaments.

Silicates

The use of pulverized crystalline *sodium silicate* as a heat stabilizer and iron inhibitor has been reported by Alexander[18], and the same author has also described[19] the use of calcium, barium, strontium, lead and silver silicates. The only two to attain widespread commercial usage, however, are *lead* and *calcium silicates*. The lead silicates are of value in that they are more transparent than other lead stabilizers and give an improved power-factor and insulation-resistance to vinyl compounds.

Lead silicate

When prepared as a frit (powdered glass) lead silicate is not a stabilizer for vinyl chloride polymers. A precipitate made by double decomposition of solutions of lead acetate and sodium silicate, however, is a very good heat stabilizer. It is difficult to prepare on account of the fineness of the precipitate, but the addition of a little barium acetate[20] helps to coagulate the suspension and improve filtering. Repeated washing of the precipitate improves the electrical properties of the stabilizer. Lead silicate is most readily incorporated in vinyl compounds in the form of a dispersion in plasticizer. This is, however, subject to settling out.

Lead silicate-silica gel co-precipitates

A number of co-precipitated lead orthosilicate-silica gel compositions are now available on both sides of the Atlantic. They give better transparency than most of the lead stabilizers, and combine moderately good heat and light stability with easier dispersion than ordinary lead silicate. They are made in a range of lead contents, having different refractive indices to suit various compounds. (The closer the refractive index of the stabilizer to that of the base, the more transparent the resulting compound.) The lead silicate-silica gel types are of particular value in highly coloured cable masses, where basic white lead carbonate has too high a pigmentary value and gives flat colours.

Proprietary brands: (1) 60% PbO: 40% SiO_2, R.I. 1·67 sp. gr. 4·60, for vinyl-vinylidene chloride co-polymers. (U.S.)—Plumb-O-Sil A[14], (U.K.)—Lead-Sil A[21]. (2) 50% PbO: 50% SiO_2, R.I. 1·58, sp. gr. 3·30, for vinyl chloride-acetate copolymers. (U.S.)—Plumb-O-Sil B[14], (U.K.)—Lead-Sil B[21].

Other types include Plumb-O-Sil C and D[14].

Basic white lead silicate (sp. gr. 5·8)

Unlike the ordinary silicate, the basic salt is opaque. It is a better heat stabilizer than the orthosilicate and is a moderate light stabilizer. It is recommended for cable masses.

Proprietary brands (U.S.): BWLS 201[22], BWLS 202[22] (with 5% mineral oil), Tribase Z[13].

A basic lead silicate-sulphate complex is also available in the U.S. and finds use as a stabilizer for cable compounds. It is, however, subject to yellowing in the presence of phosphate plasticizers. It is marketed as Tribase E[13].

Calcium silicate

Used as a white reinforcing filler for rubber, calcium silicate was tried for the same purpose in vinyl compounds and found to act as a heat stabilizer. It is also a satisfactory filler, though it has no reinforcing action on vinyls.

Proprietary brand (U.S.): Silene EF.

Salts of the sulphur acids

According to Doolittle[23] stabilizer should be capable of forming insoluble chlorides and should be reducing agents. On the question of reducing properties he adduces as evidence for this statement the fact that *lead sulphite* ($PbSO_3$) and *basic lead sulphate* ($3PbO.PbSO_4$) are both superior to *lead sulphate* ($PbSO_4$) as heat stabilizers. He also claims that a mixture of lead sulphite and basic lead sulphate is particularly effective. There would appear to be a synergetic action between them. If so, it is unusual to find two stabilizers having the same metallic radicle exhibiting synergesis. Doolittle's patent covers the use of "sublimed blue lead" (a mixture of basic lead sulphate, lead sulphite, and lead sulphide with a trace of zinc oxide) as a heat stabilizer.

The thiosulphates have been suggested as stabilizers by Chaban[24], in view of their antioxidant and reducing action. Examples include *sodium thiosulphate* $Na_2S_2O_3.5H_2O$, and the lead, barium, calcium and potassium salts.

Sodium and *potassium monosulphides* have also been proposed as stabilizers for vinyl co-polymers [25].

Tribasic lead sulphate: ($3PbO.PbSO_4.H_2O$: sp. gr. 7·1)

The only sulphur salt of any commercial importance in the stabilizer field. It is a powerful acid acceptor which has gained wide acceptance as a stabilizer for cable insulation and sheathing compounds. It has excellent electrical properties. Unlike basic white lead carbonate, there is no danger of gas evolution on overheating. A white pigment, it affords some protection against ultra-violet light, but its pigmentation limits its use to opaque compounds. It should not be used with oil-type extenders.

Proprietary brand (U.S.): Tribase[14].

Antimony oxide (Sb_2O_3)

This material is very widely used as a fire retardant, and in this connection its use is rapidly growing, especially in view of the present shortage of tritolyl phosphate, for vinyl coal conveyor belts. It has also been described[27] as a light stabilizer for chloride acetate co-polymers. It is difficult to assess to what property of the oxide, other than its opacity, this is due.

The use of *sodium-*, *calcium-* and *tertiary butyl hypochlorites* has been proposed[26] for the decolorization by oxidation of heat degraded vinyl stocks. Strictly speaking such an action is not stabilization, as it does not retard the decomposition, but merely disguises its effects.

Salts of organic acids

Stabilizers giving great clarity and freedom from haze can be prepared by fusing together *cadmium* or *lead acetate* and *sodium acetate*[28]. The resulting glass is powdered for use as a stabilizer for vinyl lacquers. *Sodium* and *potassium antimony tartrates* are also described[29] as good heat stabilizers and iron inhibitors; particularly for vinyl-chloride-maleate and chloride-fumarate co-polymers.

Young and Quattlebaum have disclosed[30] the use of basic metal chelate derivatives of 1,3-dicarbonylic substances capable of keto-enol tautomerism. One of these substances has attained commercial usage:—

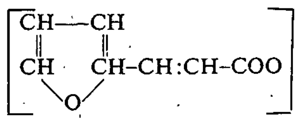
Calcium ethyl acetoacetate

This is a non-toxic light stabilizer, though not of great value when used alone; it is an excellent component of synergetic mixtures, especially with dibutyl tin dilaurate. The mixture is an economic way of using the organotins, as optimum heat and light stability is obtained with a major proportion of the calcium salt.

Proprietary brand (U.S.): C-2.[31]

The conjugated double bond system of the α-β, γ-δ unsaturated acids provides a means of getting a Diels-Alder type ring synthesis with the polyene formed by the thermal dehydrochlorination of p.v.c. This is the basis of Grummitt's patent[32] covering the alkali and alkaline earth salts of α-β, γ-δ unsaturated five-carbon acids, such as *calcium*

sorbate $(CH_3\text{-}CH{:}CH\text{-}CH{:}CH\text{-}COO)_2Ca$ and *barium α furyl acrylate*



Another unsaturated carboxylic acid, salt, capable of dienophilic activity and lately come into commercial use is:

Tribasic lead maleate $\left.\begin{matrix}CH\text{–}COOPb\text{–}O\\ CH\text{–}COOPb\text{–}O\end{matrix}\right\rangle Pb.H_2O$.

This material combines the basicity and heat stabilizing action of the more common lead stabilizers with the dienophilic colour preserving action of the maleic acid derivatives. It is one of the few really good all-round stabilizers based on lead.

Proprietary brand (U.S.): Trimal.[14]

Salicylates

The salicylate group has the useful property of being opaque to ultra-violet light and transparent to visible light. This permits the use of salicylates as ultra-violet filters in transparent compounds, thus inhibiting the catalytic oxidative decomposition of vinyl polymers. The alkaline earth salts of nuclear substituted salicylic acids,[33] e.g., *barium di-isopropyl salicylate*, have the advantage of being plasticizer-soluble. *Magnesium, strontium, calcium*[34] and *stannous*[35] *salicylates* are good heat stabilizers, particularly for long-term moderate-temperature conditions in addition to their U.V. barrier properties. Potassium salicylate is useless and ammonium salicylate is a de-stabilizer.

Lead salicylate $(C_6H_4(OH)COO)_2Pb$: sp. gr. 2·36)

This is the most commonly used salicylate stabilizer for vinyls, with the possible exception of phenyl salicylate. It is a moderate heat stabilizer but it is best used in combination with a basic stabilizer such as basic lead phthalate or lead silicate-silica gel. On account of its high refractive index (1·78) it is not suitable for transparent vinyl stocks, though it has little pigmentary power and is therefore suitable for the production of brightly coloured compounds. It gives satisfactory results with phosphate plasticizers and petroleum type plasticizer-extenders.

Proprietary brand (U.S.): Normasal.[14]

Phthalates

The metal phthalates have also been used as stabilizers for p.v.c., one of the main attractions being their ready compatibility. Stannous phthalate[35] has been suggested, but the most commonly used is:—

Dibasic lead phthalate $(2PbO.Pb.C_6H_4(COO)_2\tfrac{1}{2}H_2O$: sp. gr. 4·6))

This stabilizer combines good acid acceptance with some U.V. absorption power. It is readily dispersed in vinyl formulations, especially those plasticized with phthalate esters. Its heat stability is diminished by the presence of phosphate plasticizers.

Proprietary brand (U.S.): Dythal.[14]

Other metal salts which have been proposed include the lead salt of *n*-decyl succinic acid methyl half ester.[37]

Metal compounds other than salts

Alcoholates

The use of alcoholates has been claimed[38] to prolong the colour-free period of heated vinyl compounds and to improve their general stability. Alkaline earth metal salts of aliphatic and aromatic alcohols, including phenols, can be used. *Calcium methylate* is suggested.

Metal derivatives of nitro-alkanes

Fincke[39] has suggested the use of alkali and alkaline earth salts of nitro-substituted alkanes as high temperature colour-inhibiting stabilizers for vinyls. Examples include the salts of 1-nitropropane, nitromethane, nitroethane and 3-nitro-*n*-butane.

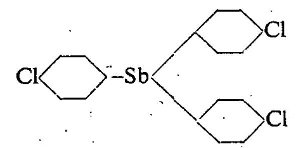
Cadmium dilauryl mercaptide

This material has recently been introduced[40] as a heat stabilizer for transparent calendering stocks. It is claimed to give heat stability and freedom from colour for long periods at the comparatively high temperatures encountered in high-speed calendering. Because of its good compatibility it does not interfere with materials such as dicetyl ether which are used as water-vapour barrier agents in packaging films. It is claimed that material stabilized with cadmium dilauryl mercaptide has been held at 350°F for 60 minutes on a calender without deleterious effects.

Proprietary brand (U.S.): ST-100.[41]

Among other metal compounds may be mentioned the *sodium, lead* and *zinc* salts of 2, 4-*dihydroxyquinoline* which may be used as heat stabilizers[42] and the alkali, alkaline earth and lead amides and imides, especially *lead phthalimide*,[43] *lead p-toluene sulphonamide*[44] and *barium o-sulphobenzimide*.[45]

The use of traces of (below 95 parts per million) of ferric chloride or ferrous sulphate has been suggested by Cheney.[46]

Tri-p-chlorphenyl stibine 

is claimed as a powerful U.V. absorber for p.v.c. and co-polymers, which can be added to the monomer and which is said to improve the heat stabilizer of the resulting polymer.[47]

A rather unusual material has been suggested as a heat and light stabilizer by Mincher and Safford[48] in *lead trimethyl silanoate*

$$\begin{array}{ccc} CH_3 & & CH_3 \\ | & & | \\ CH_3\text{–}Si & \text{–O–Pb–O–} & Si\text{–}CH_3 \\ | & & | \\ CH_3 & & CH_3 \end{array}$$

PART III. THE ORGANOMETALLIC COMPOUNDS

The history of the use of organo-metallic compounds as stabilizers for vinyl polymers begins on December 31st, 1936, with a patent application[49] by Victor Yngve, of the Carbide and Carbon Chemicals Corporation, in respect of "Organo-metallic aryl and aklyl-aryl derivatives of lead and tin." Examples quoted in this specification include *tetraphenyl tin* (which is now used as a stabilizer for chlorinated transformer oils) and *propyl triphenyl tin*.

Yngve's next patents on the subject concern trialkyl and triaryl tin and lead hydroxides and oxides,[50] the alkyl and aryl lead fatty acid salts,[51] and the tetra-alkyl tins.[52]

The dialkyl and diaryl lead carboxylic acid salts are then discussed,[53] and, finally, in a patent granted in January, 1943,[54] the first of the commercial organotin vinyl stablizers, dibutyl tin dilaurate, makes its appearance in a specification which covers the alkyl and aryl tin carboxylic acid salts.

Organotin carboxylic acid salts

Dibutyl tin dilaurate (*di-n-butyl dilauroyl dioxystannane*) (sp. gr. 1·05, m.p. (pure) 25°C, m.p. (comml) 0°C)

$$(C_4H_9)_2Sn(OOC.C_{11}H_{23})_2$$

Commercial production began in the early nineteen forties and large-scale manufacture is now carried on by three firms, two in the United States and one in this country. Its properties have been fully described[55, 56, 57]. It is still the most widely used of the organotin stabilizers, and, now that the patents covering it have lapsed, it is to be expected that its usage will increase. Its main applications are in the production of highly-plasticized, crystal-clear extrusion and moulding stocks, plastisols and organosols. It has severe

limitations in applications involving high temperatures, for which it has been largely superseded by the newer types of organotin compound.

The commercial material is deliberately manufactured from a fatty acid containing other members of the series in addition to lauric, in order to obtain a product which remains liquid under all normal conditions. The liquid is miscible with the common plasticizers and can therefore be used for plastisols, organosols, lacquers and spraying compositions without fear of the stabilizer settling out or causing gelling (of plastisols) or flocculation (of organosols). Unlike the soap stabilizers it does not increase the viscosity of plastisols. No official statement has been made on its toxicological properties, but considerable private research has been carried out. It would appear that the dose required to produce symptoms of poisoning is so large that there is virtually no danger of harmful effects resulting from the minute amounts which could be extracted by an aqueous fluid from, for example, an organotin-stabilized vinyl hose.

Proprietary brands: (U.K.) Stanclere DBTL[58]; (U.S.) D-22[31]; (U.S.) RS-12[59].

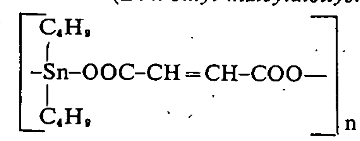
Dibutyl tin diacetate (*Di-n-butyldiacetoxystannane*) (sp. gr. 1·31, m.p. 5-10°C)

$(C_4H_9)_2Sn(OOC.CH_3)_2$

This material is similar in properties to the laurate, but it is less stable and so much more volatile that it now finds little, if any, use as a vinyl stabilizer.

Proprietary brands (U.S.): RS-1.[59]

Dibutyl tin maleate (*Di-n-butyl maleyldioxystannane*) (M.P. c.110°C)



In 1943, Quattlebaum and Noffsinger[60] stated that the organotin salts of α, β-unsaturated carboxylic acids would react with the coloured polyenes present in heat-degraded vinyl polymers, thus preserving the natural water-white colour of the resin. The most important stabilizer in this group is dibutyl tin maleate. It is a better colour-inhibitor than dibutyl tin dilaurate for short-term, high-temperature processing, owing to this dienophilic activity.

It is, however, a polymeric material, and one in which difficulty is experienced in manufacturing to a controlled degree of polymerization. The low polymers are very volatile and the fumes evolved from such processes as open-roll milling are dangerously vesicant.

The high polymers, on the other hand, while much less volatile, are also much less efficient as stabilizers. Unlike the laurate and acetate, the maleate is a solid, and more difficult, on account of its sticky, resinous nature, to disperse in the vinyl premix. It is also somewhat incompatible with vinyl compounds and has a tendency to plate out in calendering.

Proprietary brands (U.S.): RS-13[59], D-14.[31]

Hydrocarbon tin alcoholates

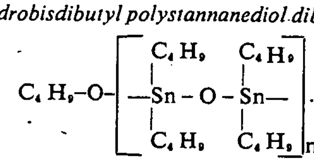
The next type of organotin stabilizer to appear (1948) was the hydrocarbon tin alcoholate. Burt's patent[61] describes the use as heat and light stabilizers of the dibutyl tin alcoholates of unsaturated alcohols, including allyl, benzyl and furfuryl alcohols. It is believed that some proprietary organotin stabilizers are based on this type of compound, but no positive identification has been revealed by the manufacturers.

Polymeric organotins

One of the difficulties in preparing a practical organotin stabilizer is the problem of selecting an optimum alkyl chain length. The long chain fatty acids tend to give an incompatible product, while the short chain types are too volatile, and also, on account of their higher tin content, too expensive.

An ingenious solution was arrived at by Advance Solvents & Chemical Corporation. The first of the Advance organotin compounds was,

Anhydrobisdibutyl polystannanediol dibutyl ester (sp. gr. 1·15)



The organotin dialkoxides or polystannanediols were disclosed in patents by Mack and Parker[62, 63]. By using a polymeric compound high volatility was avoided, and long-term heat stability ensured; by using a relatively short alkyl chain the compatibility was kept comparatively high. The esters[64] are an improvement on the alcohols.

This stabilizer is soluble in hot plasticizers, which aids its dispersion in the vinyl compound. Its cold solubility in ketones is useful in the preparation of organosols. It is satisfactory at high temperatures and for fairly long periods in plasticized stocks, but less useful in unplasticized compounds.

Proprietary brand (U.S.): Stabilizer 3[65].

Anhydropolystannanediol-dialkyl tin halide complexes

One of the stages in the manufacture of the dialkyl tin dicarboxylic acid salts is the dialkyl tin halide. These dihalides are generally believed to be antagonistic to the action of the stabilizers, though the present author has reason to doubt this. It is, however, the accepted practice to ensure that organotin stabilizers are manufactured in a halide-free form. This involves expensive procedures which are reflected in the cost of the finished product. According, however, to Mack,[56] effective stabilizers may be prepared by forming oxonium compounds between polystannanediols and dialkyl tin halides. These can be prepared by refluxing a dialkyl tin oxide with a dialkyl tin halide. As dilakyl tin oxides are prepared by ammonia hydrolysis of the halides, this is a very convenient process. The halide is partially hydrolysed, giving oxide and a calculated proportion of unchanged halide. The mixture is refluxed in benzene or xylene containing a trace of moisture. The oxide then forms a polystannanediol which reacts with the dihalide to form an oxonium complex which may be represented by the structure:—$RO(Sn(R'_2)O)_nR.SnR'_2X_2$ of which an example is polymeric *dibutyl tin dimethoxide-dibutyl tin dichloride* $CH_3O\text{-}(Sn(C_4H_9)_2O)_nCH_3.(C_4H_9)_2SnCl_2$

Sulphur-containing organotins

The earliest patent on a sulphur-containing organotin as a stabilizer for vinyl resins was that granted to Schlattman[67] in 1948 in respect of the dialkyl tin salts of *o*-sulphobenzimide. This was followed by a reference to *tetra-alpha-thienyl tin* which claimed as a good heat and light stabilizer for transparent compounds.

Organotin sulphonamides

More recently, Mack and Parker have taken out a patent[69] on the organotin sulphonamides of the general formula $R_xSn(R'NO_2SR'')_y$ where R, R', and R″ are alkyl or aryl radicals and $x+y=4$. These materials are plasticizers as well as stabilizers, and in reacting with hydrochloric acid they split off sulphonamides, which are compatible with vinyl resins. Examples of this type of compound include *dibutyl tin dibenzene sulphonamide* $(C_4H_9)_2Sn(HNO_2S.C_6H_5)_2$

These stabilizers appear to have a very considerable future. They are particularly satisfactory for unplasticized extrusion compounds, where the fact that the residue from the reaction is an efficient flux (plasticizer at high temperature, with

little action at roor
Proprietary bran
this type, though n
Other thio-organ
Thermolite 31 m
composition of this
The possibility
suggested by Mack

Miscellaneous orga
Organotin oxide-est
The production
taken either by the
synthesis. In either
oxide. In 1951 Ca
covery that the org
very satisfactory as
ordinary ester plas
effective heat and
technique is simply
together, in molar p
hour. The mixture
liquid product wh
Analysis shows no
complexes include d
preferably, complex
ester plasticizers.
Trialkyl tin mon
improvement on the
It is claimed that g
product being a l

1. Japs, A. B., U.S.I
2. Temple, S., U.S.P
3. Costa, J. E., and
4. Schaeffer, H. L., a
-9; B.P. 660,165,
5. Chaban, C. J., U.
6. R. T. Vanderbilt
U.S.A.
7. Victor Chemical
8. *Chemical Industrie*
9. Huff C. E., and Z
10. Ferro Chemical C
11. B.P. 707,338 (14/4
12. B.P. 692,967 (17/6
13. National Lead Co
14. National Lead Co.
15. Chaban, C. J., U.
16. Harwick Standard
17. Mouchiroud, A. F
18. Alexander, C. H.,
19. Alexander, C. H.,
20. Taft, G. H., U.S.P
21. Associated Lead
Minories, London,
22. Eagle-Picher Co.,
23. Doolittle, A. K., U
24. Chaban, C. J., U.S
25. Cox, F. W., and W
26. Tucker, H., U.S.P
27. Doolittle, A. K., U
28. Young, D. M., an
29. Cox, F. W., and W
30. Young, D. M., an
31. Carbide & Carbon
York 17, N.Y., U.
32. Grummitt, O. J., U
33. Croft-White, P. G.
34. Cox, F. W., and W
35. Chertoff, G. J., B.
36. Hendricks, J. G.,
687,425.

little action at room temperature) is a great advantage.

Proprietary brand (U.S.): Advance M-17[65] is probably of this type, though no confirmation is available.

Other thio-organotin compounds on the market include Thermolite 31 marketed by Metal and Thermit. The composition of this material is a trade secret.

The possibility of using organotin sulphones has been suggested by Mack and Parker.[70]

Miscellaneous organotin compounds

Organotin oxide-ester plasticizer complexes

The production of organotin compounds can be undertaken either by the Grignard route or by the Wurtz-Fittig synthesis. In either case one of the stages is the dialkyl tin oxide. In 1951 Carroll applied for a patent[71] on his discovery that the organotin oxides, which are not themselves very satisfactory as stabilizers, could be reacted with the ordinary ester plasticizers to give materials which were effective heat and light stabilizer for vinyl resins. The technique is simply to heat the oxide and the plasticizer together, in molar proportions, with agitation, for about an hour. The mixture at first solidifies, and then gives a clear liquid product which is soluble in ethers and ketones. Analysis shows no production of alcohol or ether. Suitable complexes include dibutyl tin oxide-di-octyl phthalate, and, preferably, complexes of organotin oxides with maleate ester plasticizers.

Trialkyl tin monoalkoxides have been proposed[72] as an improvement on the dibutyl tin dilaurate type of stabilizer. It is claimed that greater clarity is obtained, the reaction product being a lower alkyl alcohol and a trialkyl tin chloride, both of which are soluble in the vinyl compound to a greater degree than is lauric acid.

Organotin malonic ester compounds, and organotin diketo compounds have recently been suggested by Mack.[70] Earlier suggestions have included dibutyl diphenyl tin[72, 73] as a component of synergetic mixtures.

It is not surprising, in view of the relatively high cost of the organotin compounds, that considerable study has been devoted to their synergetic action with other types of stabilizer. It is hoped to publish some observations in due course on this important topic.

Proprietary organotin stabilizers

A number of materials are on sale which contain organotin compounds of which the composition has not been revealed. These include:

- Stanclere 10[58] a low-cost synergetic mixture.
- Stanclere 20, a non-toxic synergetic mixture.
- Stanclere 30, an organosol light-stabilizer.
- Stanclere 60, a modified dibutyl tin dilaurate.
- Stanclere 70, a new high-temperature stabilizer.
- Advance OM 10[65], stabilizer for rigid compounds.
- Advance OM 18, concentrated version of OM 10.
- Advance 52, stabilizer for "crystal-clear" stocks.
- Advance 52-16, concentrated version of 52.

Organolead compounds

Interest in these materials has diminished in favour of the organotins, presumably in view of the toxicity of the lead compounds. Triethyl lead hexyl maleate, however, has been suggested[75] as a synergist for dibutyl diphenyl tin.[74]

References

1. Japs, A. B., U.S.P. 2,218,645.
2. Temple, S., U.S.P. 2,482,038.
3. Costa, J. E., and McIntyre, O. R., B.P. 694,474.
4. Schaeffer, H. L., and Havens, C. B., U.S.P. 2,477,656, -7, -8, -9; B.P. 660,165, -6, -7.
5. Chaban, C. J., U.S.P. 2,507,142, -3; B.P. 653,822.
6. R. T. Vanderbilt Co., 230 Park Avenue, New York 17, N.Y., U.S.A.
7. Victor Chemical Co.
8. *Chemical Industries*, 1942, 51-1, p. 516.
9. Huff C. E., and Zimmerman, G. A., U.S.P. 2,499,503.
10. Ferro Chemical Co., Bedford, Ohio, U.S.A.
11. B.P. 707,338 (14/4/54).
12. B.P. 692,967 (17/6/53).
13. National Lead Co. Bulletin on "Dyphos."
14. National Lead Co., 111 Broadway, New York 6, N.Y., U.S.A.
15. Chaban, C. J., U.S.P. 2,487,099.
16. Harwick Standard Chemical Co., Akron, Ohio, U.S.A.
17. Mouchiroud, A. F. G., U.S.P. 2,535,649.
18. Alexander, C. H., U.S.P. 2,174,545.
19. Alexander, C. H., U.S.P. 2,179,973.
20. Taft, G. H., U.S.P. 2,378,739.
21. Associated Lead Manufacturers, Ltd., Crescent House, Minories, London, E.C.3.
22. Eagle-Picher Co., Cincinatti 1, Ohio, U.S.A.
23. Doolittle, A. K., U.S.P. 2,161,024.
24. Chaban, C. J., U.S.P. 2,566,791.
25. Cox, F. W., and Wallace, J. M., U.S.P. 2,478,862.
26. Tucker, H., U.S.P. 2,333,280.
27. Doolittle, A. K., U.S.P. 2,161,026.
28. Young, D. M., and Quattlebaum, W. M., U.S.P. 2,161,611.
29. Cox, F. W., and Wallace, J. W., U.S.P. 2,461,531.
30. Young, D. M., and Quattlebaum, W. M., U.S.P. 2,307,075.
31. Carbide & Carbon Chemical Corp., 30 East 42nd Street, New York 17, N.Y., U.S.A.
32. Grummitt, O. J., U.S.P. 2,544,142.
33. Croft-White, P. G., and Garner, P. J., B.P. 617,620.
34. Cox, F. W., and Wallace, J. M., U.S.P. 2,438,102.
35. Chertoff, G. J., B.P. 674,164.
36. Hendricks, J. G., and Ratti, H. J., U.S.P. 2,608,547; B.P. 687,425.
37. Safford, M. M., U.S.P. 2,455,879.
38. Quattlebaum, W. M., U.S.P. 2,256,625.
39. Fincke, J. K., U.S.P. 2,464,177.
40. Stevens, A. H., B.P. 647,970.
41. Firestone Plastics Co., Pottstown, Pa., U.S.A.,
42. Lewis, J. R., et al, U.S.P. 2,338,187.
43. Scott, W., U.S.P. 2,319,953.
44. Scott, W., U.S.P. 2,319,954.
45. Schlattman, R. H., U.S.P. 2,455,612.
46. Cheney, H. A., U.S.P. 2,563,772.
47. Park, H. F., U.S.P. 2,456,565.
48. Mincher, E. L., and Safford, M. M., B.P. 629,332.
49. Yngve, V., U.S.P. 2,219,463.
50. Yngve, V., U.S.P. 2,267,777.
51. Yngve, V., U.S.P. 2,267,778.
52. Yngve, V., U.S.P. 2,267,779.
53. Yngve, V., U.S.P. 2,307,090.
54. Yngve, V., U.S.P. 2,307,092.
55. Smith, H. V., *Plastics*, 17, 264, 1952.
56. Pure Chemicals, Ltd., Technical Bulletin A2.
57. Metal & Thermit Corp. Tech. Data Sheet 101.
58. Pure Chemicals, Ltd., Kirkby Trading Estate, Liverpool.
59. Metal & Thermit Corp., 100 East 42nd Street, New York 17, N.Y., U.S.A.
60. Quattlebaum, W. M., and Noffsinger, C. A., U.S.P. 2,307,157.
61. Burt, S. L., U.S.P. 2,489,518; B.P. 679,655.
62. Mack, G. P., U.S.P. 2,510,035.
63. Mack, G. P., and Parker, E., U.S.P. 2,592,926.
64. Mack, G. P., and Parker, E., U.S.P. 2,628,211.
65. Advance Solvents & Chemical Corp., 245 5th Avenue, New York 16., N.Y., U.S.A.
66. Mack, G. P., U.S.P. 2,604,460.
67. Schlattman, R. H., U.S.P. 2,455,613.
68. Fincke, J. W., and Gluesenkamp, E. W., U.S.P. 2,479,918.
69. Mack, G. P., and Parker, E., U.S.P. 2,618,625.
70. Mack, G. P., and Parker, E., U.S.P. 2,604,483.
71. Carroll, R. T., U.S.P. 2,597,920.
72. Cleverdon, D., et al, U.S.P. 2,623,892.
73. Leininger, R. I., U.S.P. 2,476,422.
74. Richard, W. R., U.S.P. 2,477,349.
75. Baer, M., U.S.P. 2,561,044.